REFRACTORIES FOR GLASS PRODUCTION

UDC 666.1.031.29:666.76

DEVELOPMENT OF REFRACTORY COMPOSITE MATERIALS FOR GLASS PRODUCTION

N. N. Shcherbakova,[1] G. S. Rossikhina,[1] L. L. Chernina,[1] P. K. Zheltov,[1] and M. V. Ivanova[1]

Translated from Steklo i Keramika, No. 1, pp. 16 – 18, January, 2006.

The Semiluki Refractory Works produces refractories according to the technology of concrete and keeps developing compositions and refining the technology for producing large-size products by vibromolding. The Saratov Institute of Glass has performed service testing of concrete samples and determined their physicomechanical characteristics. The testing of samples fired at temperatures not higher than 1000°C has demonstrated their rather high compressive strength (from 40 to 60 N/mm^2).

The decreasing volume of chamotte refractories produced by ramming in Russia has made it necessary to develop new refractory mixtures suitable for state-of-the-art mechanized molding technologies (vibromolding and vibrocasting) and that impart to the products strength sufficient for transportation and installation without using high-temperature firing and still preserve all refractory service properties. Refractory concretes, which are nonfired composites with refractoriness 1700°C and higher, have been known and used in glass production for over 30 years. Such concrete consists of a refractory filler and a binding material (binder) curing at a normal or increased temperature and having limited shrinkage at service temperatures. The type of the binder is selected based on the properties that the product should posses, i.e., a constant volume and a sufficient strength in the entire temperature interval: from ambient to service temperatures [1]. High-alumina cement with water acting as a dispersion medium can be conveniently used as a binder for refractory concrete. High-alumina cement is classified as a hydration-curing binder, in which the curing process proceeds with formation of hydrates:

$$3(CaO \cdot Al_2O_3) + H_2O \rightarrow$$
$$3CaO \cdot Al_2O_3 \cdot 6H_2O + 5Al(OH)_3 + H_2O.$$

Due to the formation of hydrates, the strength of refractory concrete varies depending on heat treatment temperature. Under relatively low curing temperatures (around 300°C) the strength grows, whereas in the interval of 400 – 1000°C mainly determined by the dehydration of the binder and the loss of chemically bound water the strength decreases (the strength drop) [2]. As the temperature increases above 1000°C, the process of sintering starts and the strength increases. The strength of refractory concrete depends on the strength of the filler, the binder, the contact phase, and especially on the existence of shrinkage, thermal, and other stresses. Destructive forces in concrete do not always lead to crack formation, since stresses in concrete are nonuniformly distributed and concentrate on components with a high elasticity modulus, i.e., the filling components; consequently, high strength of the filler determines high strength of the concrete. Concrete produced by vibration molding typically has a filler of enhanced coarseness (up to 6 – 8 mm). Cracks in fact do not propagate across the product thickness; emerging cracks become arrested on the filler grains. This is a positive property of vibromolded concrete, since in ramming technology, due to the presence of cracks going in different directions, a nonuniform distribution of pores and filler grains, etc., gas permeability may differ in different sites of the same product.

A refractory in glass production is subjected to heavy duty. The material is required to retain its physicomechanical characteristics for a long time: up to 5 – 9 years in a glass-melting furnace and up to 25 years in a tin melt tank; moreover, perceptible gas emission and chemical interaction with the aggressive medium is not allowed, since it degrades the quality of glass. To increase the resistance of a refractory, it should have minimum porosity, a small pore size, and have virtually no channel porosity and gas permeability, since the

[1] Saratov Institute of Glass, Saratov, Russia; Semiluki Refractory Works, Semiluki, Novgorod Region, Russia; Saratov State Technical University, Saratov, Russia.

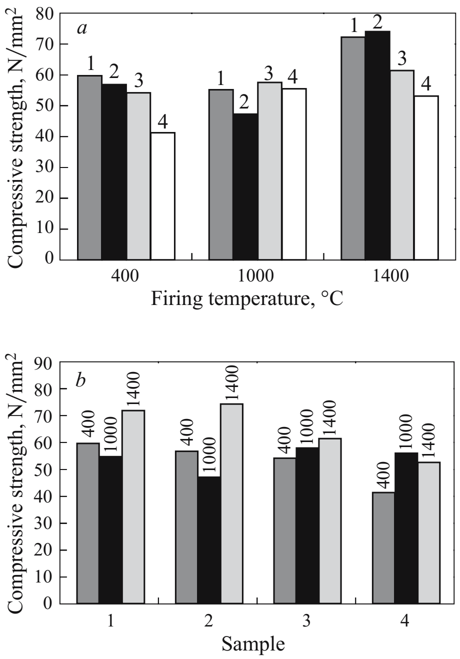

Fig. 1. Compressive strength of samples of different compositions (1 – 4) formed at the same temperature (*a*) and its variation with firing temperature increasing from 400 to 1400°C (*b*).

latter facilitates the emission of gas bubbles which cause defects on glass surfaces.

When a porous refractory is used in a tank with a tin melt, liquid melt may become absorbed by the solid body with open pores. Although a more porous material has a higher thermal resistance, it is less capable of withstanding the destructive effect of slag and salts, less heat-conducting, and has lower mechanical strength [3]. Therefore, significant factors for selecting refractories for glass-producing lines are the nature of the refractory, its chemical and mineralogical composition, and its physicomechanical properties. Refractory materials for the bottom of the tin melt tank are especially critical. Although they are not subjected to a high temperature impact, they function in constant contact with molten metal. If the metal penetrates into the pores, the refractory brickwork enters in chemical reactions with the metal, which leads to the dissolution of the refractory.

The durability of a refractory largely depends on its thermal resistance, which improves with increasing thermal conductivity. Consequently, refractory under heavy duty is required to have the maximum possible thermal conductivity. However, the bottom of the tank with molten tin should have a temperature not higher than 200°C, and the temporary difference across the refractory bottom bars is up to 800°C in the hot zone of the tank, which is too high for a chamotte material. Concrete precisely has better thermal resistance compared to rammed products, such as chamotte bars for the melt tank, even when they have the same type of refractory basis, in our case aluminosilicate basis. The thermal conductivity

TABLE 1

Composition	Mass content, %					Thermal conductivity,* W/(m · K), of samples fired up to 1000°C
	Al_2O_3	TiO_2	Fe_2O_3	SiO_2	CaO	
1	51.70	1.17	0.80	43.50	2.20	1.53
2	47.20	1.10	0.60	51.50	1.90	1.48
3	44.40	1.60	1.20	49.00	2.40	1.13
4	43.95	1.64	1.16	48.60	2.18	1.15

* Determined at the average temperature of 525°C.

of concretes should not differ much from that of chamotte refractories. Seals in brickwork are always zones of destruction. Therefore, refractories, especially large-size products, should have clearly defined shapes and minimal shrinkage. It follows from the above that the choice of refractory material should be performed bearing in mind all the above-mentioned requirements, including the purpose and the service temperature of the refractory [4].

The Semiluki Refractory Works not only produces refractory concrete, but keeps developing and refining new compositions and technologies for vibromolding of refractories. Samples of low-cement fire-resistant concrete of grade VShS based on a chamotte filler (using an integral matrix system) produced by vibration molding have been supplied to the Saratov Institute of Glass for industrial testing and determining their physicochemical characteristics applied to service in a melt tank lining on a float-glass line. The chemical composition of refractory mixtures is given in Table 1.

In order to determine shrinkage properties, samples that had undergone primary heat treatment at the manufacturing company not higher than 400°C were fired in a gas furnace in oxidizing conditions according to a temperature schedule identical to the schedule of heating the melt tank to 1000°C. No linear increase was registered in samples after cooling. Some of the samples were subjected to high-temperature firing up to 1400°C.

The testing of physicomechanical properties was carried out according to standard methods on cube-shaped samples with a side length of 100 and 60 mm. To determine the type of concrete least susceptible to the destructive effect of dehydration, the samples were tested for compressive strength; next, their open porosity and apparent density was determined after their firing up to the maximum temperatures of 400, 1000, and 1400°C. Samples of concrete after heat treatment at different maximum temperatures were tested in service conditions in a melt tank at the Saratov Institute of Glass.

All samples showed sufficient compressive strength: over 40 N/mm^2 (Fig. 1*a*). Regardless of heat treatment, the highest strength was registered in samples 1 – 3 fired up to 1400°C. The least strength variation with increasing firing temperature was registered in sample 3 (Fig. 1*b*), which

shows that the dehydration of the binder material in firing up to 1000°C proceeds without strength loss. The apparent density of samples 3 and 4 also grows smoothly and insignificantly with increasing firing temperature while their open porosity decreases from 20 – 21 to 16 – 18%, respectively. The physicomechanical parameters of materials 1 and 2 deteriorate sharply after firing up to 1000°C, which indicates their strength loss as a consequence of dehydration.

The channel porosity and gas impermeability of materials VShS is significantly lower than that of chamotte materials produced by ramming, which explains the obvious advantage of products made of VShS refractory. Apparently vibration molding does not lead to the formation of channel pores; pores are present in the material in the form of enclosed cavities. Among VShS materials, in terms of thermal conductivity samples 3 and 4 (the lower thermal conductivity) made of VShS material are preferred (Table 1).

Thus, variations in the properties of VShS materials of composition 3 was the firing temperature varies from 400 to 1400°C are less significant than in other materials considered; consequently, it is the most suitable for applications without high-temperature firing.

The compressive strength and linear thermal variations of products made of the considered VShS materials fully satisfy the standard requirements; therefore, they can be used for installation of refractory lining either after primary heat treatment up to 400°C carried out at the manufacturing plant and subsequent firing in the process of heating up, or after firing up to 1400°C at the manufacturing plant.

REFERENCES

1. Yu. E. Pivinskii, “New generation of refractory concretes, low-cement concrete, and cast vibration thixotropic refractory mixtures,” *Ogneupory*, No. 7, 1 – 10 (1990).
2. K. K. Strelov, *Theoretical Principles of Technology of Refractory Materials* [in Russian], Metallurgiya, Moscow (1985).
3. E. Ya. Litovskii and I. G. Fedina, “Analysis of the dependence of thermal conductivity of refractories of the system $Al_2O_3 – SiO_2$ on their composition and porosity in the temperature interval of 400 – 1600°C,” in: *Coll. Papers “Refractories: Technology and Properties”* [in Russian], Metallurgiya, Moscow (1985), pp. 75 – 82.
4. N. N. Shcherbakova and L. L. Chernina, “The practice of Saratov Institute of Glass in developing special refractories for the float process,” *Steklo Keram.*, No. 5, 12 – 13 (2005).